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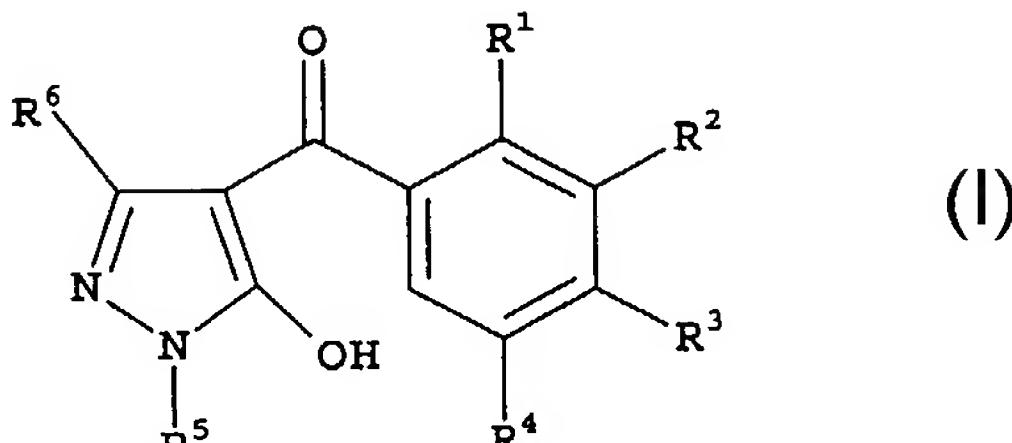
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(54) Title: SYNERGISTICALLY ACTING HERBICIDAL MIXTURES



including imazapyr, imazaquin, imazamethabenz-methyl, imazamox, imazapic and imazethapyr; or one of its environmentally compatible salts; and, if desired, C) at least one further herbicidal compound; in a synergistically effective amount. Compositions comprising these mixtures, processes for the preparation of these compositions, and their use for controlling undesired plants

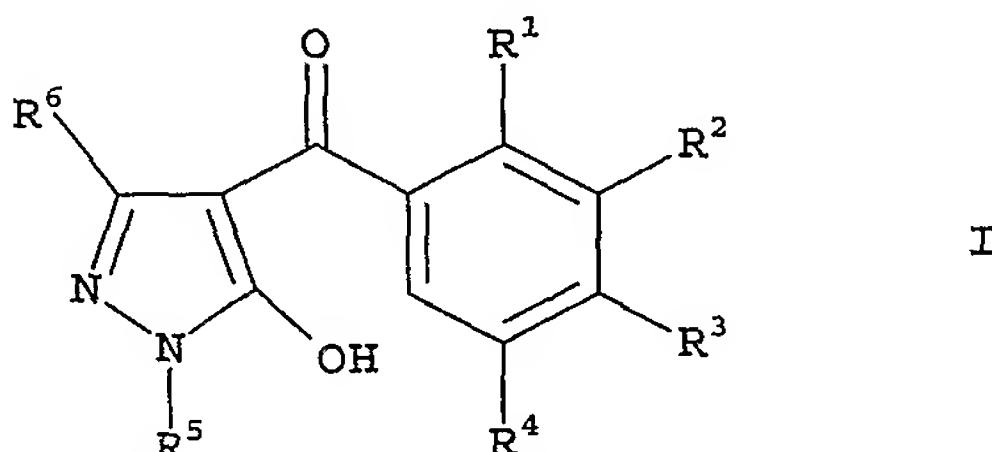
(57) Abstract: A synergistic herbicidal mixture comprising: A) at least one 3-heterocyclyl-substituted benzoyl derivative of the formula (I) in which the variables have the following meanings: R¹, R³ are halogen, alkyl, haloalkyl, alkoxy, haloalkoxy, alkylthio, alkylsulfinyl or alkylsulfonyl; R² is a optionally substituted heterocyclic radical selected from the group: isoxazol-3-yl, isoxazol-4-yl, isoxazol-5-yl, 4,5-dihydroisoxazol-3-yl, 4,5-dihydroisoxazol-4-yl and 4,5-dihydroisoxazol-5-yl; R⁴ is hydrogen, halogen or alkyl; R⁵ is alkyl; R⁶ is hydrogen or alkyl; or one of its environmentally compatible salts; and B) two herbicides selected from the group

Synergistically acting herbicidal mixtures

The present invention relates to a synergistic herbicidal mixture comprising

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A) at least one 3-heterocyclyl-substituted benzoyl derivative of the formula I



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in which the variables have the following meanings:

R¹, R³ are halogen, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy, C₁-C₆-alkylthio, C₁-C₆-alkylsulfinyl or C₁-C₆-alkylsulfonyl;

15

R² is a heterocyclic radical selected from the group: iso-xazol-3-yl, isoazol-4-yl, isoazol-5-yl, 4,5-dihydro-isoazol-3-yl, 4,5-dihydroisoazol-4-yl and 4,5-dihydroisoazol-5-yl; it being possible for the six radicals mentioned to be unsubstituted or mono- or polysubstituted by halogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkyl, C₁-C₄-haloalkoxy or C₁-C₄-alkylthio;

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R⁴ is hydrogen, halogen or C₁-C₆-alkyl;

R⁵ is C₁-C₆-alkyl;

R⁶ is hydrogen or C₁-C₆-alkyl;

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or one of its environmentally compatible salts;

and

B) two herbicides selected from the group including imazapyr, imazaquin, imazamethabenz-methyl, imazamox, imazapic and imazethapyr;

5 or one of its environmentally compatible salts;

and, if desired,

C) at least one herbicidal compound from the group of the acetyl-CoA carboxylase inhibitors (ACC), acetolactate synthase inhibitors (ALS), amides, auxin herbicides, auxin transport inhibitors, carotenoid biosynthesis inhibitors, enolpyruvyl-shikimate 3-phosphate synthase inhibitors (EPSPS), glutamine synthetase inhibitors, lipid biosynthesis inhibitors, mitosis inhibitors, protoporphyrinogen IX oxidase inhibitors, photosynthesis inhibitors, synergists, growth substances, cell wall biosynthesis inhibitors and a variety of other herbicides;

20 in a synergistically effective amount.

The invention furthermore relates to herbicidal compositions comprising a herbicidally active amount of a synergistic herbicidal mixture as defined above and at least one liquid and/or solid carrier and, if desired, at least one surfactant.

Moreover, the invention relates to processes for the preparation of these compositions and to a method of controlling undesirable vegetation.

30 In crop protection products, it is always desirable to increase the specific activity of an active ingredient and the reliability of action. It is an object of the present invention to increase the activity and/or selectivity of the herbicidally active 3-heterocyclyl-substituted benzoyl derivatives of the formula I against undesirable harmful plants.

We have found that this object is achieved by the mixtures defined at the outset. We have furthermore found herbicidal compo-

sitions which comprise these mixtures, processes for their preparation, and methods of controlling undesirable vegetation. In the last-mentioned cases, it is irrelevant whether the herbicidally active compounds of the components A), B) and, if desired, C) are formulated and applied jointly or separately and in which sequence they are applied in the case of separate application.

The mixtures according to the invention show a synergistic effect; the compatibility of the herbicidally active compounds of components A), B) and, if desired, C) for certain crop plants is generally retained.

Suitable components C are, as acetyl-CoA carboxylase inhibitors (ACC), for example, cyclohexenone oxime ethers, phenoxyphenoxy-propionic esters or arylaminopropionic acids. The acetolactate synthase inhibitors (ALS) include, inter alia, imidazolinones, pyrimidyl ethers, sulfonamides or sulfonyl ureas. Relevant auxin herbicides are, inter alia, pyridine carboxylic acids, 2,4-D or benazolin. Lipid biosynthesis inhibitors which are used are, inter alia, anilides, chloroacetanilides, thioureas, benfuresate or perfluidone. Suitable mitosis inhibitors are, inter alia, carbamates, dinitroanilines, pyridines, butamifos, chlorthal-dimethyl (DCPA) or maleic hydrazide. Examples of protoporphyrinogen IX oxidase inhibitors are, inter alia, diphenyl ethers, oxadiazoles, cyclic imides or pyrazoles. Suitable photosynthesis inhibitors are, inter alia, propanil, pyridate, pyridafol, benzothiadiazinones, dinitrophenols, dipyridylenes, ureas, phenols, chloridazon, triazine, triazinone, uracils or biscarbamates. The synergists are, inter alia, oxiranes. Examples of suitable growth substances are aryloxyalkanoic acids, benzoic acids or quinolinecarboxylic acids. The group "various other herbicide" is to be understood as meaning, inter alia, the classes of the active ingredients dicloropropionic acids, dihydrobenzofurans, phenylacetic acids and individual herbicides mentioned below whose mechanism of action is not (fully) understood.

Other suitable components C) are active compounds selected from the group of the amides, auxin transport inhibitors, carotenoic

biosynthesis inhibitors, enolpyruvylshikimate 3-phosphate synthase inhibitors (EPSPS), glutamine synthetase inhibitors and cell wall synthesis inhibitors.

5 Examples of herbicides which can be used in combination with the 3-heterocyclyl-substituted benzoyl derivatives of formula I and the compound of formula II according to the present invention are, *inter alia*:

10 C1 acetyl-CoA carboxylase inhibitors (ACC), for example

- cyclohexenone oxime ethers, such as aloxydim, clethodim, cloproxydim, cycloxydim, sethoxydim, tralkoxydim, butroxydim, clefoxydim or tepraloxydim;
- phenoxyphenoxypropionic esters, such as clodinafop-propargyl (and, if appropriate, cloquintocet), cyhalofop-butyl, diclofop-methyl, fenoxaprop-ethyl, fenoxaprop-P-ethyl, fenthiapropethyl, fluazifop-butyl, fluazifop-P-butyl, haloxyfop-ethoxyethyl, haloxyfop-methyl, haloxyfop-P-methyl, isoxapryifop, propaquizafop, quinalofop-ethyl, quinalofop-P-ethyl or quinalofop-tefuryl; or
- arylaminopropionic acids, such as flamprop-methyl or flamprop-isopropyl;

25 C2 acetolactate synthase inhibitors (ALS), for example

- imidazolinones, such as imazapyr, imazaquin, imazamethabenz-methyl (imazame), imazamox, imazapic, imazethapyr or imazamethapyr;
- pyrimidyl ethers, such as pyrithiobac-acid, pyrithiobac-sodium, bispyribac-sodium, KIH-6127 or pyribenzoxym;
- sulfonamides, such as florasulam, flumetsulam or metosulam; or
- sulfonylureas, such as amidosulfuron, azimsulfuron, bensulfuron-methyl, chlorimuron-ethyl, chlorsulfuron, cinosulfuron, cyclosulfamuron, ethametsulfuron-methyl, ethoxysulfuron, flazasulfuron, halosulfuron-methyl, imazosulfuron, metsulfuron-methyl, nicosulfuron, primisulfuron-methyl, prosulfuron, pyrazosulfuron-

ethyl, rimsulfuron, sulfometuron-methyl, thifensulfuron-methyl, triasulfuron, tribenuron-methyl, triflusulfuron-methyl, N-[[[4-methoxy-6-(trifluoromethyl)-1,3,5-triazin-2-yl]amino]carbonyl]-2-(trifluoromethyl)-benzenesulfon-amide, sulfosulfuron or iodosulfuron;

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C3 amides, for example

- allidochlor (CDAA), benzoylprop-ethyl, bromobutide, chlorthiamid, diphenamid, etobenzanid (benzchlomet), fluthiamide, fosamin or monalide;

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C4 auxin herbicides, for example

- pyridinecarboxylic acids, such as clopyralid or picloram; or
- 2,4-D or benazolin;

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C5 auxin transport inhibitors, for example

- naptalame or diflufenzopyr;

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C6 carotenoid biosynthesis inhibitors, for example

- benzofenap, clomazone (dimethazone), diflufenican, fluorochloridone, fluridone, pyrazolynate, pyrazoxyfen, isoxaflutole, isoxachlortole, mesotrione, sulcotrione (chlormesulone), ketospiradox, flurtamone, norflurazon or amitrol;

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C7 enolpyruvylshikimate-3-phosphate synthase inhibitors

(EPSPS), for example

- glyphosate or sulfosate;

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C8 glutamine synthetase inhibitors, for example

- bilanafos (bialaphos) or glufosinate-ammonium;

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C9 lipid biosynthesis inhibitors, for example

- anilides, such as anilofos or mefenacet;
- chloroacetanilides, such as dimethenamid, S-dimethenamid, acetochlor, alachlor, butachlor, butenachlor, diethyl-ethyl, dimethachlor, metazachlor, metolachlor,

S-metolachlor, pretilachlor, propachlor, prynachlor, terbuchlor, thenylchlor or xylachlor;

- thioureas, such as butylate, cycloate, di-allate, dimethylpiperate, EPTC, esprocarb, molinate, pebulate, prosulfofocarb, thiobencarb (benthiocarb), tri-allate or vernolate; or
- benfuresate or perfluidone;

C10 mitosis inhibitors, for example

- carbamates, such as asulam, carbetamid, chlorpropham, orbencarb, pronamid (propyzamid), propham or tiocarbazil;
- dinitroanilines, such as benefin, butralin, dinitramin, ethalfluralin, fluchloralin, oryzalin, pendimethalin, prodiame or trifluralin;
- pyridines, such as dithiopyr or thiazopyr; or
- butamifos, chlorthal-dimethyl (DCPA) or maleic hydrazide;

C11 protoporphyrinogen IX oxidase inhibitors, for example

- diphenyl ethers, such as acifluorfen, acifluorfen-sodium, aclonifen, bifenox, chlornitrofen (CNP), ethoxyfen, fluorodifen, fluoroglycofen-ethyl, fomesafen, furyloxyfen, lactofen, nitrofen, nitrofluorfen or oxyfluorfen;
- oxadiazoles, such as oxadiargyl or oxadiazon;
- cyclic imides, such as azafenidin, butafenacil, carfentrazone-ethyl, cinidon-ethyl, flumiclorac-pentyl, flumioxazin, flumipropyn, flupropacil, fluthiacet-methyl, sulfentrazone or thidiazimin; or
- pyrazoles, such as ET-751, JV 485 or nipyraprofen;

C12 photosynthesis inhibitors, for example

- propanil, pyridate or pyridafol;
- benzothiadiazinones, such as bentazone;
- dinitrophenols, for example bromofenoxim, dinoseb, dinoseb-acetate, dinoterb or DNOC;
- dipyridylanes, such as cyperquat-chloride, difenzoquat-methylsulfate, diquat or paraquat-dichloride;

- ureas, such as chlorbromuron, chlorotoluron, difenoxuron, dimefuron, diuron, ethidimuron, fenuron, fluometuron, isoproturon, isouron, linuron, methabenzthiazuron, methazole, metobenzuron, metoxuron, monolinuron, neburon, siduron or tebuthiuron;
- phenols, such as bromoxynil or ioxynil;
- chloridazon;
- triazines, such as ametryn, atrazine, cyanazine, desmetryn, dimethamethryne, hexazinone, prometon, prometryn, propazine, simazine, simetryn, terbumeton, terbutryn, terbutylazine or trietazine;
- triazinones, such as metamitron or metribuzin;
- uracils, such as bromacil, lenacil or terbacil; or
- biscarbamates, such as desmedipham or phenmedipham;

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C13 synergists, for example

- oxiranes, such as tridiphane;

C14 growth substances, for example

- aryloxyalkanoic acids, such as 2,4-DB, clomeprop, di-chlorprop, dichlorprop-P (2,4-DP-P), fluoroxypyrr, MCPA, MCPB, mecoprop, mecoprop-P or triclopyr;
- benzoic acids, such as chloramben or dicamba; or
- quinolonecarboxylic acids, such as quinchlorac or quinmerac;

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C15 cell wall synthesis inhibitors, for example

- isoxaben or dichlobenil;

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C16 various other herbicides, for example

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- dichloropropionic acids, such as dalapon;
- dihydrobenzofurans, such as ethofumesate;
- phenylacetic acids, such as chlorfenac (fenac); or
- aziprotryn, barban, bensulide, benzthiazuron, benzo-fluor, buminafos, buthidazole, buturon, cafenstrole, chlorbufam, chlorfenprop-methyl, chloroxuron, cin-methylin, cumyluron, cycluron, cyprazine, cyprazole, dibenzyluron, dipropetryn, dymron, eglinazin-ethyl, endothall, ethiozin, flucabazole, fluorbentranil, flu-

poxam, isocarbamid, isopropalin, karbutilate, meflu-
idide, monuron, napropamide, napropanilide, nitralin,
oxaciclomefone, phenisopham, piperophos, procyzaine,
profluralin, pyributicarb, secbumeton, sulfallate
5 (CDEC), terbucarb, triaziflam, triazofenamid or trime-
turon;

or their environmentally compatible salts.

10 The 3-heterocyclyl-substituted benzoyl derivatives of the for-
mula I are disclosed in WO 96/26206, WO 97/41116, WO 97/41117,
WO 97/41118 and WO 98/31681.

15 The herbicidally active compounds from amongst groups B and C1
to C16 are described, for example, in

- "Herbicide [Herbicides]", Hock, Fedtke, Schmidt, 1st edi-
tion, Thieme 1995 (s. "quinclorac" p. 238, "molinat" p. 32,
"butachlor" p. 32, "pretilachlor" p. 32, "dithiopyr" p. 32,
20 "mefenacet" p. 32, "fenoxapropethyl" p. 216, "dimepiperate"
p. 32, "pyrazolynate" p. 146, "pyrazoxyfen" p. 146, "bensul-
furonmethyl" p. 31, "pyrazosulfuron-ethyl" p. 31, "cinosul-
furon" p. 31, "benfuresate" p. 233, "bromobutide" p. 243,
"dymron" p. 243, "dimethyametryn" p. 118, "esprocarb" p.
25 229, "pyributicarb" p. 32, "cinemthylin" p. 32, "propanil"
p. 32, "2,4-D" p. 30, "bentazon" p. 30, "azimsulfuron (DPX-
A-8947)" p. 175, "mecoprop-P" p. 237, "chlorpropham" p. 205,
"ethoxyfen" p. 30, "haloxyfop-P-methyl" p. 38, "haloxyfop-
ethoxyethyl" p. 38, "flumiclorac-pentyl" p. 35, "flu-
30 propacil" p. 143, "nipyrapclofen" p. 145, "metosulam" p. 33,
"ethametsulfuron-methyl" p. 36, "thifensulfuron-methyl" p.
35 35, "pyrithiobac acid" p. 181);
- "Agricultural Chemicals", Book II Herbicides, 1993 (s.
35 "thiobencarb" p. 85, "benzofenap" p. 221, "napropanilid" p.
49, "piperophos" p. 102, "anilofos" p. 241, "imazosulfuron
(TH-913)" p. 150, "etobenzamid (HW-52)" p. 54, "sulcotrione
(ICIA-0051)" p. 268, "poast" p. 253, "focus" p. 222, "di-
methenamid" p. 48, "sulfosate" p. 236, "2,4-DB" p. 10, "di-

chlorprop-P" p. 6, "flupoxam" p. 44, "prosulfocarb" p. 84, "quinmerac" p. 233, "metazachlor" p. 64, "flurtamone" p. 265, "bromofenoxim" p. 228, "fomesafen" p. 248, "imazamethabenz-methyl" p. 153, "clodinafop-propargyl" p. 214, "fenoxaprop-P-ethyl" p. 208, "fluazifop-P-butyl" p. 207, "quizalofop-P-ethyl" p. 210, "quizalofop-terfuryl" p. 211, "flumioxazin" p. 43, "flumipropyn" p. 267, "sulfentrazone" p. 261, "thiazopyr" p. 226, "pyrithiobac-sodium" p. 266, "flumetsulam" p. 227, "amidosulfuron" p. 151, "halosulfuron-methyl" p. 148, "rimsulfuron" p. 138, "tribenuron-methyl" p. 139, "triflusulfuron-methyl" p. 137, "primisulfuron-methyl" p. 147);

- "Agricultural Chemicals", Book II Herbicides, 13th Edition (s. "carfenstole" p. 284, "sulfosulfuron" p. 145, "ethoxy-sulfuron" p. 149, "pyribenzoxy" p. 279, "diflufenzopyr" p. 90, "ET-751" p. 278, "carfentrazone-ethyl" p. 267, "fluthiacet-methyl" p. 277, "imazapic" p. 160, "butenachlor" p. 54, "tiocarbazil" p. 84, "fluthiamide" p. 62, "isoxaflutole" p. 283, "butroxydim" p. 259,)

- "Short Review of Herbicides & PGRs 1991, Hodogaya Chemicals (s. "furyloxyfen" p. 142, "triazofenamid" p. 268, "thenyl-chlorid (NSK-850)" p. 52, "cumyluron (JC-940)" p. 90, "pendimethalin (AC-92553)" p. 58, "buthidazole" p. 88, "cyprazole" p. 38, "allidochlor" p. 48, "benzoylprop-ethyl" p. 38, "chlorthiamid" p. 150, "diphenamid" p. 34, "flamprop-methyl" p. 40, "fosamin" p. 232, "isoxaben" p. 42, "mon-alide" p. 32, "naptalam" p. 36, "pronamid" p. 34, "bia-laphos" p. 234, "glufosinate-ammonium" p. 234, "glyphosate" p. 232, "amitrol" p. 254, "clomeprop" p. 20, "dichlorprop" p. 6, "fenoprop" p. 8, "fluroxypyr" p. 156, "MCDA" p. 4, "MCDB" p. 8, "mecoprop" p. 6, "napropamide" p. 16, "triclopyr" p. 154, "chloramben" p. 28, "dicamba" p. 26, "clomazone" p. 268, "diflufenican" p. 42, "fluorochloridone" p. 266, "fluridone" p. 156, "asulam" p. 12, "barban" p. 100, "butylate" p. 106, "carbetamide" p. 6, "chlorobufam" p. 100, "cycloate" p. 108, "desmedipham" p. 104, "di-allate" p. 106, "EPTC" p. 108, "orbencarb" p. 112, "pebulate" p. 106,

"phenisopham" p. 118, "phenmedipham" p. 104, "propham" p. 100, "sulfallate" p. 110, "terbucarb" p. 102, "tri-allate" p. 108, "vernolate" p. 108, "acetochlor" p. 48, "alachlor" p. 46, "diethathyl-ethyl" p. 48, "dimethachlor" p. 50, "metolachlor" p. 46, "propachlor" p. 44, "pyrnachlor" p. 44, "terbuchlor" p. 48, "xylachlor" p. 52, "alloxydim" p. 260, "c lethodim" p. 270, "cloproxydim" p. 268, "tralkoxydim" p. 270, "dalapon" p. 212, "ethofumesate" p. 124, "benefin" p. 54, "butralin" p. 58, "dinitramin" p. 56, "ethalfluralin" p. 60, "fluchloralin" p. 54, "isopropalin" p. 58, "nitralin" p. 58, "oryzalin" p. 60, "prodiamine" p. 62, "profluralin" p. 54, "trifluralin" p. 54, "dinoseb" p. 128, "dinoseb-acetate" p. 128, "dinoterb" p. 128, "DNOC" p. 126, "acifluorfen-sodium" p. 142, "aclonifen" p. 146, "bifenox" p. 140, "chlornitrofen" p. 138, "difenoxyuron" p. 76, "fluorodifen" p. 138, "fluoroglycofen-ethyl" p. 146, "lactofen" p. 144, "nitrofen" p. 136, "nitrofluorfen" p. 140, "oxyfluorfen" p. 140, "cyperquat-chloride" p. 158, "difenoquat-methylsulfate" p. 160, "diquat" p. 158, "paraquat-dichloride" p. 158, "benzthiazuron" p. 82, "buturon" p. 66, "chlorbromuron" p. 72, "chloroxuron" p. 76, "chlorotoluron" p. 74, "cycluron" p. 84, "dimefuron" p. 88, "diuron" p. 70, "ethidimuron" p. 86, "fenuron" p. 64, "fluometuron" p. 68, "isoproturon" p. 80, "isouron" p. 88, "karbutilate" p. 76, "linuron" p. 72, "methabenzthiazuron" p. 82, "metoxuron" p. 72, "monolinuron" p. 66, "monuron" p. 64, "neburon" p. 72, "siduron" p. 68, "tebuthiuron" p. 86, "trimeturon" p. 64, "isocarbamid" p. 168, "imazamethapyr" p. 172, "imazapyr" p. 170, "imazaquin" p. 170, "imazethapyr" p. 172, "methazole" p. 162, "oxadiazon" p. 162, "tridiphane" p. 266, "bromoxynil" p. 148, "ioxynil" p. 148, "diclofop-methyl" p. 16, "fenthiaprop-ethyl" p. 20, "fluazifop-butyl" p. 18, "haloxyfop-methyl" p. 18, "isoxapryifop" p. 22, "propaquizafop" p. 24, "quizalofop-ethyl" p. 20, "chlorfenac" p. 258, "chlorfenprop-methyl" p. 258, "chloridazon" p. 174, "maleic hydrazide" p. 162, "norflurazon" p. 174, "pyridate" p. 176, "clopyralid" p. 154, "picloram" p. 154, "chlorimuron-ethyl" p. 92, "chlorsulfuron" p. 92, "flazasulfuron" p. 96, "metsulfuron-methyl" p. 92, "nicosulfuron" p. 96, "sulfometu-

ron-methyl" p. 92, "triasulfuron" p. 94, "ametryn" p. 198, "atrazine" p. 188, "aziprotryne" p. 206, "cyanazine" p. 192, "cyprazine" p. 192, "desmetryne" p. 200, "dipropetryn" p. 202, "eglinazine-ethyl" p. 208, "hexazinone" p. 208, "procyclazine" p. 192, "prometone" p. 196, "prometryn" p. 196, "propazine" p. 188, "secbumeton" p. 196, "simazine" p. 188, "simetryn" p. 196, "terbumeton" p. 204, "terbutryn" p. 198, "terbutylazine" p. 190, "triethylazine" p. 188, "ethiozine" p. 210, "metamitron" p. 206, "metribuzin" p. 202, "bromacil" p. 180, "lenacil" p. 180, "terbacil" p. 180, "benazolin" p. 262, "bensulide" p. 228, "benzofluor" p. 266, "butamifos" p. 228, "DCPA" p. 28, "dichlobenil" p. 148, "endothal" p. 264, "mefluidide" p. 306, "perfluidone" p. 260, "terbucchlor" p. 48);

15

- "Global Herbicide Directory" First Edition, 1994 (s. "oxadiargyl" p. 96);
- "European Directory of Agrochemical Products" Volume 2 - Herbicides" Fourth Edition (s. "buminafos" p. 255).
- "The Pesticide Manual, 12th edition, 2000 (s. "bispipyribac-sodium" p. 97, "florasulam" p. 420, "cyclosulfamuron" p. 217, "pretilachlor" p. 755)

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Moreover, the compound "DEH-112" is disclosed in European Patent Application EP-A 302 203. The compound "tepraloxydim" is described in DE-A 33 36 140; the compound "cinidon-ethyl" in DE-A 36 03 789 and the compound "fluorbentranil" in EP-A 84 893.

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Other compounds are known from "Brighton Crop Protection Conference - Weeds - 1993" (s. "thidiazimin" p. 29, "AC-322140" p. 41, "KIH-6127" p. 47, "prosulfuron" p. 53, "KIH-2023" p. 61, "metobenzuron" p. 67). The compound "carfenstrole (CH-900)" is mentioned in EP-A 332 133, and the compound N-[[[4-methoxy-6-(trifluoromethyl)-1,3,5-triazin-2-yl]amino]-carbonyl]-2-(trifluoromethyl-benzenesulfonamide) is described in PCT/EP 96/03996.

The assignment of the active ingredients to the respective mechanisms of action is based on current knowledge. If several

mechanisms of action apply to one active ingredient, this substance was only assigned to one mode of action.

The 3-heterocyclyl-substituted benzoyl derivatives of the formula I can exist, or be used, in the form of the pure enantiomers and also as racemates or diastereomer mixtures.

The 3-heterocyclyl-substituted benzoyl derivatives of the formula I and/or the herbicidally active compounds from amongs group B and/or the herbicidally active compounds from amongs groups C1 to C16 may also exist in the form of their environmentally compatible salts. Suitable salts are, in general, the salts of those cations, or the acid addition salts of those acids, whose cations, or anions, respectively, do not adversely affect the herbicidal action of the active ingredients.

Suitable cations are, in particular, ions of the alkali metals, preferably lithium, sodium and potassium, of the alkaline earth metals, preferably calcium and magnesium, and of the transition metals, preferably manganese, copper, zinc and iron, and also ammonium, it being possible in this case, if desired, for one to four hydrogen atoms to be replaced by C₁-C₄-alkyl, hydroxy-C₁-C₄-alkyl, C₁-C₄-alkoxy-C₁-C₄-alkyl, hydroxy-C₁-C₄-alkoxy-C₁-C₄-alkyl, phenyl or benzyl, preferably ammonium, isopropylammonium, di-25 methylammonium, diisopropylammonium, tetramethylammonium, tetra-butylammonium, 2-(2-hydroxyeth-1-oxy)eth-1-yl ammonium, di(2-hydroxyeth-1-yl)ammonium, trimethylbenzylammonium, furthermore phosphonium ions, sulfonium ions, preferably tri(C₁-C₄-alkyl)-sulfonium and sulfoxonium ions, preferably, tri(C₁-C₄-alkyl)-sulfoxonium.

Anions of suitable acid addition salts are mainly chloride, bromide, fluoride, hydrogen sulfate, sulfate, dihydrogen phosphate, hydrogen phosphate, nitrate, hydrogen carbonate, carbonate, hexafluorosilicate, hexafluorophosphate, benzoate and the anions of C₁-C₄-alkanoic acids, preferably formate, acetate, propionate and butyrate.

Preferred with regard to the synergistic herbicidal action of the mixtures according to the invention are those 3-heterocyclyl-substituted benzoyl derivatives of the formula I in which the variables have the following meanings, either alone or in combination:

5 R¹ halogen such as chlorine or bromine, C₁-C₆-alkyl such as methyl or ethyl or C₁-C₆-alkylsulfonyl such as methylsulfonyl or ethylsulfonyl;

10 especially preferably chlorine, methyl or methylsulfonyl;

15 R² a heterocyclic radical selected from the group: isoxazol-3-yl, isoxazol-5-yl and 4,5-dihydroisoxazol-3-yl, it being possible for the three radicals mentioned to be unsubstituted or monosubstituted by halogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkyl, C₁-C₄-haloalkoxy or C₁-C₄-alkylthio;

20 especially preferably isoxazol-5-yl, 3-methyl-isoxazol-5-yl, 4,5-dihydroisoxazol-3-yl, 5-methyl-4,5-dihydroisoxazol-yl, 5-ethyl-4,5-dihydroisoxazol-3-yl or 4,5-dimethyl-4,5-dihydroisoxazol-3-yl;

25 R³ halogen such as chlorine or bromine or C₁-C₆-alkylsulfonyl such as methylsulfonyl or ethylsulfonyl; especially preferably chlorine, methylsulfonyl or ethylsulfonyl;

30 R⁴ hydrogen or methyl; especially preferably hydrogen;

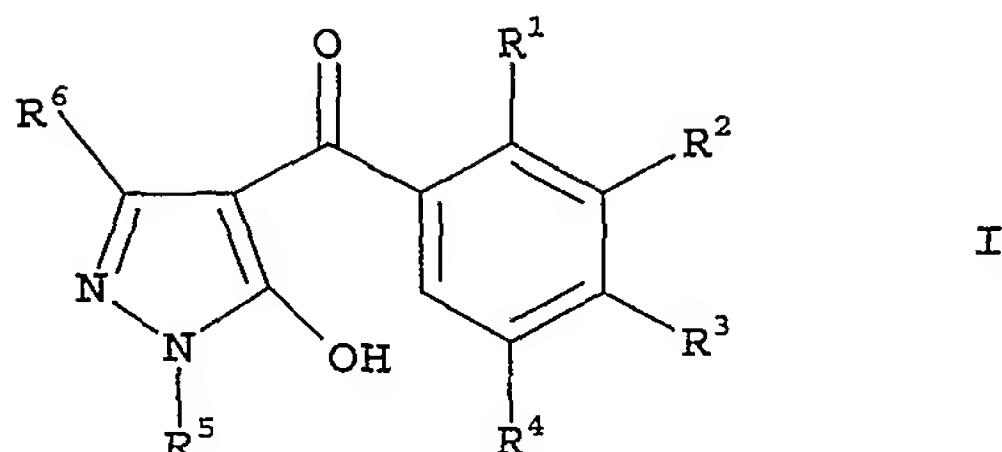
35 R⁵ is C₁-C₆-alkyl, such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl or 2-methylpropyl; especially preferably methyl, ethyl or 1-methylethyl;

40 R⁶ hydrogen or C₁-C₆-alkyl, such as methyl or ethyl; especially preferably hydrogen or methyl.

Very particularly preferred are those 3-heterocyclyl-substituted benzoyl derivatives of the formula Ia, in particular the com-

pounds Ia.1 to Ia.47, which are mentioned in Table 1 which follows:

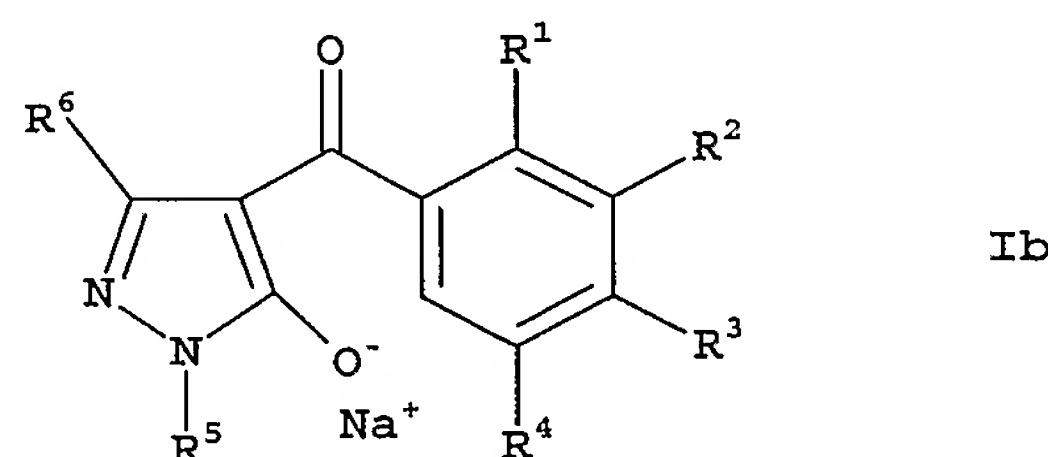
5 Table 1



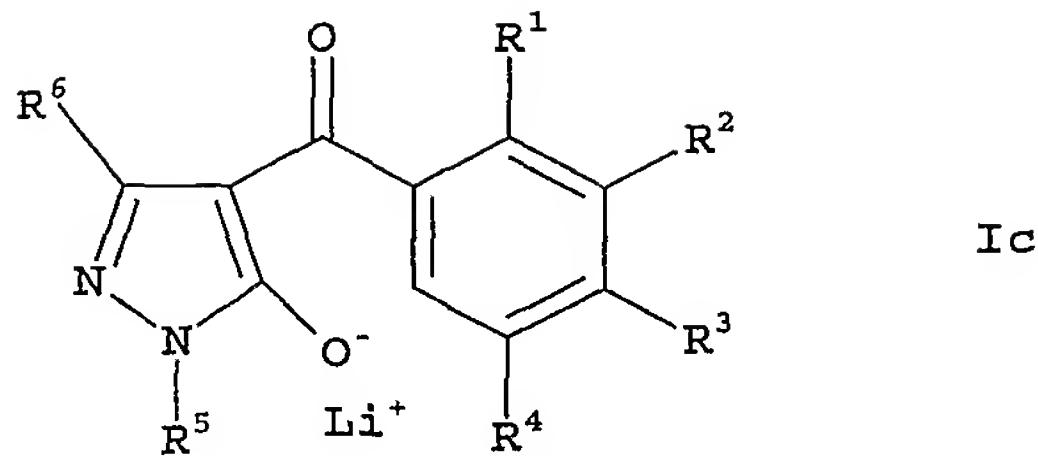
No.	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶
Ia.1	Cl	4,5-dihydroisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	CH ₃
Ia.2	Cl	4,5-dihydroisoxazol-3-yl	Cl	H	CH ₃	CH ₃
Ia.3	Cl	4,5-dihydroisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.4	Cl	4,5-dihydro-5-methylisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.5	Cl	4,5-dihydro-5,5-dimethylisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.6	Cl	4,5-dihydro-5-ethylisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.7	Cl	4,5-dihydro-5,5-diethylisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.8	Cl	4,5-dihydro-5-chloromethylisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.9	Cl	4,5-dihydro-5-ethoxyisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.10	Cl	4,5-dihydro-5-methoxyisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.11	Cl	4,5-dihydro-4,5-dimethylisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.12	Cl	4,5-dihydro-5-thioethylisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.13	Cl	4,5-dihydro-5-trifluoromethylisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.14	Cl	4,5-dihydroisoxazol-3-yl	SO ₂ CH ₃	H	C ₂ H ₅	H
Ia.15	Cl	4,5-dihydroisoxazol-3-yl	Cl	H	C ₂ H ₅	H
Ia.16	Cl	4,5-dihydro-5-methylisoxazol-3-yl	SO ₂ CH ₃	H	C ₂ H ₅	H
Ia.17	Cl	4,5-dihydro-5,5-dimethylisoxazol-3-yl	SO ₂ CH ₃	H	C ₂ H ₅	H
Ia.18	Cl	4,5-dihydro-5-ethylisoxazol-3-yl	SO ₂ CH ₃	H	C ₂ H ₅	H
Ia.19	Cl	4,5-dihydro-5,5-diethylisoxazol-3-yl	SO ₂ CH ₃	H	C ₂ H ₅	H
Ia.20	Cl	4,5-dihydro-5-chloromethylisoxazol-3-yl	SO ₂ CH ₃	H	C ₂ H ₅	H
Ia.21	Cl	4,5-dihydroisoxazol-3-yl	SOCH ₃	H	C ₂ H ₅	H
Ia.22	Cl	4,5-dihydro-5-ethoxyisoxazol-3-yl	SO ₂ CH ₃	H	C ₂ H ₅	H
Ia.23	Cl	4,5-dihydro-4,5-dimethylisoxazol-3-yl	SO ₂ CH ₃	H	C ₂ H ₅	H
Ia.24	Cl	4,5-dihydro-5-thioethylisoxazol-3-yl	SO ₂ CH ₃	H	C ₂ H ₅	H
Ia.25	Cl	4,5-dihydro-5-trifluoromethylisoxazol-3-yl	SO ₂ CH ₃	H	C ₂ H ₅	H

Ia.26	Cl	4,5-dihydroisoxazol-3-yl	SO ₂ CH ₃	H	i-C ₄ H ₉	H
Ia.27	CH ₃	4,5-dihydroisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	CH ₃
Ia.28	CH ₃	4,5-dihydroisoxazol-3-yl	Cl	H	CH ₃	CH ₃
Ia.29	CH ₃	4,5-dihydroisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.30	CH ₃	4,5-dihydro-5-methylisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.31	CH ₃	4,5-dihydro-5,5-dimethylisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.32	CH ₃	4,5-dihydro-5-ethylisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.33	CH ₃	4,5-dihydro-5,5-diethylisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.34	CH ₃	4,5-dihydroisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.35	CH ₃	4,5-dihydro-4,5-dimethylisoxazol-3-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.36	CH ₃	4,5-dihydroisoxazol-3-yl	SO ₂ CH ₃	H	C ₂ H ₅	H
Ia.37	CH ₃	4,5-dihydroisoxazol-3-yl	Cl	H	C ₂ H ₅	H
Ia.38	CH ₃	4,5-dihydro-5-methylisoxazol-3-yl	SO ₂ CH ₃	H	C ₂ H ₅	H
Ia.39	CH ₃	4,5-dihydro-5,5-dimethylisoxazol-3-yl	SO ₂ CH ₃	H	C ₂ H ₅	H
Ia.40	CH ₃	4,5-dihydro-5-ethylisoxazol-3-yl	SO ₂ CH ₃	H	C ₂ H ₅	H
Ia.41	CH ₃	4,5-dihydro-5,5-diethylisoxazol-3-yl	SO ₂ CH ₃	H	C ₂ H ₅	H
Ia.42	CH ₃	4,5-dihydro-4,5-dimethylisoxazol-3-yl	SO ₂ CH ₃	H	C ₂ H ₅	H
Ia.43	CH ₃	4,5-dihydroisoxazol-3-yl	SO ₂ CH ₃	H	i-C ₄ H ₉	H
Ia.44	Cl	3-methylisoxazol-5-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.45	Cl	3-methylisoxazol-5-yl	SO ₂ CH ₃	H	C ₂ H ₅	H
Ia.46	CH ₃	3-methylisoxazol-5-yl	SO ₂ CH ₃	H	CH ₃	H
Ia.47	CH ₃	3-methylisoxazol-5-yl	SO ₂ CH ₃	H	C ₂ H ₅	H

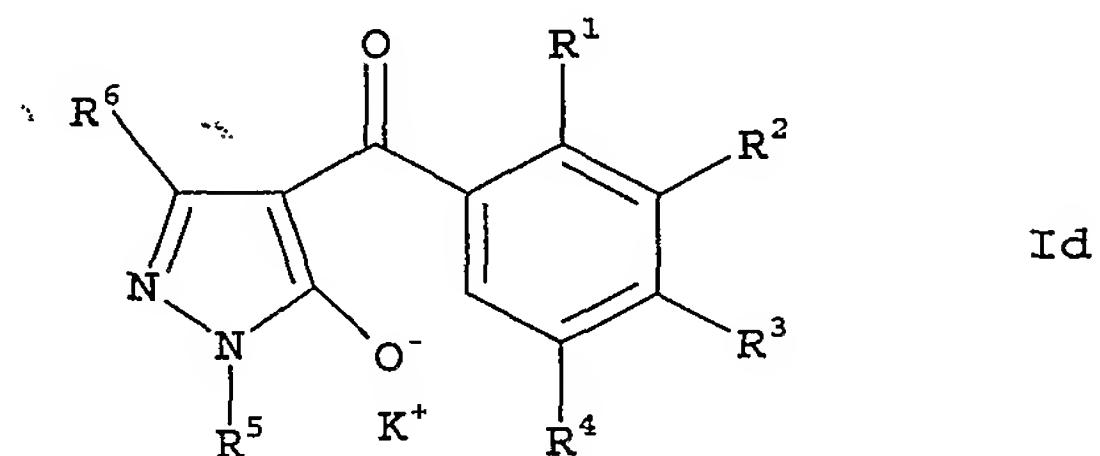
- Also very particularly preferred are the compounds Ib, in particular the compounds Ib.1 to Ib.47, which differ from the compounds Ia.1 to Ia.47 only by the fact that they are present as the sodium salt:



- Also very particularly preferred are the compounds Ic, in particular the compounds Ic.1 to Ic.47, which differ from the compounds Ia.1 to Ia.47 only by the fact that they are present as the lithium salt:



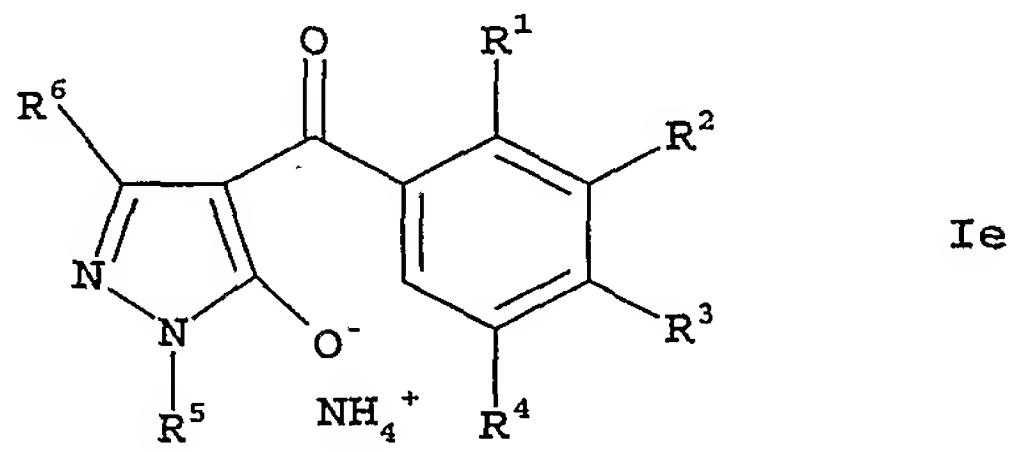
- Also very particularly preferred are the compounds Id, in particular the compounds Id.1 to Id.47, which differ from the compounds Ia.1 to Ia.47 only by the fact that they are present as the potassium salt:



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- Also very particularly preferred are the compounds Ie, in particular the compounds Ie.1 to Ie.47, which differ from the compounds Ia.1 to Ia.47 only by the fact that they are present as the ammonium salt:

15



20

- Very particularly preferred are, especially, the compounds Ia, especially the compounds Ia.1 to Ia.47.

- Very particularly preferred are, moreover, the 3-heterocyclyl-substituted benzoyl derivatives of the formula I, where

R⁴ is hydrogen.

- Very particularly preferred are, moreover, the 3-heterocyclyl substituted benzoyl derivatives of the formula I where

R² is a heterocyclic radical selected from the group: isoxazol-3-yl, isoxazol-4-yl and isoxazol-5-yl, it being possible for the three radicals mentioned to be unsubstituted or mono- or polysubstituted by halogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkyl, C₁-C₄-haloalkoxy or C₁-C₄-alkylthio.

Very particularly preferred are, especially, the 3-heterocyclyl-substituted benzoyl derivatives of the formula I, where

R² is isoxazol-3-yl which can be unsubstituted or mono- or polysubstituted by halogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkyl, C₁-C₄-haloalkoxy or C₁-C₄-alkylthio;

R⁴ is hydrogen.

Very particularly preferred are also, especially, the 3-heterocyclyl-substituted benzoyl derivatives of the formula I where

R² is isoxazol-5-yl, which can be unsubstituted or mono- or polysubstituted by halogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkyl, C₁-C₄-haloalkoxy or C₁-C₄-alkylthio;

R⁴ is hydrogen.

Most particularly preferred is 4-[2-chloro-3-(3-methyl-isoxazol-5-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole.

Most particularly preferred is also 4-[2-methyl-3-(3-methyl-isoxazol-5-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole.

5 - Very particularly preferred are, moreover, the 3-heterocyclyl-substituted benzoyl derivatives of the formula I where

10 R^2 is a heterocyclic radical selected from the group: 4,5-dihydroisoxazol-3-yl, 4,5-dihydroisoxazol-4-yl and 4,5-dihydroisoxazol-5-yl, it being possible for the three radicals mentioned to be unsubstituted or mono- or polysubstituted by halogen, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkyl, C_1 - C_4 -haloalkoxy or C_1 - C_4 -alkylthio.

15 Very particularly preferred are, especially, the 3-heterocyclyl-substituted benzoyl derivatives of the formula I where

20 R^2 is 4,5-dihydroisoxazol-3-yl which can be unsubstituted or mono- or polysubstituted by halogen, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkyl, C_1 - C_4 -haloalkoxy or C_1 - C_4 -alkylthio;

25 R^4 is hydrogen.

Most particularly preferred are the 3-heterocyclyl-substituted benzoyl derivatives of the formula I where

30 R^1 is halogen or C_1 - C_6 -alkyl; and

35 R^2 is 4,5-dihydroisoxazol-3-yl which can be unsubstituted or mono- or polysubstituted by halogen, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkyl, C_1 - C_4 -haloalkoxy or C_1 - C_4 -alkylthio;

R^3 is C_1 - C_6 -alkylsulfonyl;

R^4 is hydrogen.

Most especially preferred is 4-[2-chloro-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonylbenzoyl]-1-methyl-5-hydroxy-1H-pyrazole.

5

Most particularly preferred is also 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonylbenzoyl]-1-methyl-5-hydroxy-1H-pyrazole.

10 Preferred with regard to the synergistic herbicidal action of the mixtures according to the invention are those mixtures comprising as component B) imazapyr and imazethapyr, or imazapyr and imazapic; especially preferred are those mixtures comprising as component B) imazapyr and imazethapyr.

15

15 In a further preferred embodiment, the synergistic herbicidal mixture comprises, three herbicidal active compounds, a compound of formula I (component A) and two herbicides selected from the group including imazapyr, imazaquin, imazamethabenz-methyl, imazamox, imazapic and imazetapyr (component B).

20 - For particular preferred embodiments, the respective preferences described above apply analogously.

25 In particular the synergistic herbicidal mixture comprises as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonylbenzoyl]-1-methyl-5-hydroxy-1H-pyrazole and two herbicides selected from the group including imazapyr, imazaquin, imazamethabenz-methyl, imazamox, imazapic and imazethapyr (component B).

30 Especially the synergistic herbicidal mixture comprises as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonylbenzoyl]-1-methyl-5-hydroxy-1H-pyrazole and as component B) imazapyr and imazethapyr.

35 In a further embodiment the synergistic herbicidal mixture especially comprises as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonylbenzoyl]-1-methyl-5-

hydroxy-1H-pyrazole and as component B) imazapyr and imazapic.

In a further preferred embodiment, the synergistic herbicidal mixture comprises, at least four herbicidal active compounds, a compound of formula I (component A), two herbicides selected from the group including imazapyr, imazaquin, imazamethabenz-methyl, imazamox, imazapic and imazethapyr (component B), and

10 C) at least one herbicidal compound from the group of the acetyl-CoA carboxylase inhibitors (ACC), acetolactate synthase inhibitors (ALS), amides, auxin herbicides, auxin transport inhibitors, carotenoid biosynthesis inhibitors, enolpyruvyl-shikimate 3-phosphate synthase inhibitors (EPSPS), glutamine synthetase inhibitors, lipid biosynthesis inhibitors, mitosis inhibitors, protoporphyrinogen IX oxidase inhibitors, photosynthesis inhibitors, synergists, growth substances, cell wall biosynthesis inhibitors and a variety of other herbicides.

20 With a view to the synergistic herbicidal action of the mixtures comprising a component A), B) and C) according to the invention, compounds from amongst groups C1 to C14 or C16, preferably from amongst groups C9 and C12, are preferred as component C).

In particular, compounds from amongst the classes of active ingredients mentioned below are preferred, or the following compounds are very particularly preferred:

30 C1 acetyl-CoA carboxylase inhibitors (ACC):

- cyclohexenone oxime ethers, in particular cycloxydim, sethoxydim or tralkoxydim, preferably sethoxydim or tralkoxydim; or
- phenoxyphenoxypropionic esters, in particular clodinafop-propargyl (and, if appropriate, cloquintocet), fenoxaprop-ethyl or fenoxaprop-P-ethyl, preferably clodinafop-propargyl (and, if appropriate, cloquintocet) or fenoxaprop-P-ethyl;

C2 acetolactate synthase inhibitors (ALS):

- imidazolinones, in particular imazapyr, imazaquin, imazamethabenz, imazethapyr or imazamox, preferably imazapyr;
- pyrimidyl ethers, in particular pyrithiobac sodium;
- sulfonamides, in particular florasulam, flumetsulam or metosulam, preferably metosulam; or
- sulfonylureas, in particular halosulfuron-methyl, nicosulfuron, primisulfuron-methyl, prosulfuron, rimsulfuron, thifensulfuron-methyl, tribenuron-methyl, N-[[[4-methoxy-6-(trifluoromethyl)-1,3,5-triazin-2-yl]-amino]carbonyl]-2-(trifluoromethyl)-benzenesulfonamide or sulfosulfuron;

15

C3 amides:

- fluthiamide;

C4 auxin herbicides:

- pyridinecarboxylic acids, in particular clopyralid; or
- 2,4-D;

C5 auxin transport inhibitors:

- diflufenzopyr;

C6 carotenoid biosynthesis inhibitors:

- isoxaflutole, mesotrione, isoxachloride, ketospiradox or sulcotrione (chlormesulone), in particular isoxaflutole or sulcotrione;

C7 enolpyruvylshikimate-3-phosphate synthase inhibitors (EPSPS):

- glyphosate or sulfosate;

35

C8 glutamin synthetase inhibitors:

- glufosinate-ammonium;

C9 lipid biosynthesis inhibitors:

- chloroacetanilides, in particular dimethenamid, S-dimethenamid, acetochlor, metolachlor or S-metolachlor;
- thioureas, in particular benthiocarb;

5

C10 mitosis inhibitors:

- dinitroanilines, in particular pendimethalin;

C11 protoporphyrinogen IX oxidase inhibitors:

- diphenyl ethers, in particular acifluorfen or acifluorfen-sodium;
- oxadiazoles, in particular oxadiargyl; or
- cyclic imides, in particular butafenacil, carfentrazone-ethyl, cinidon-ethyl or flumiclorac-pentyl, preferably carfentrazone-ethyl, cinidon-ethyl or flumidorac-pentyl;
- pyrazoles, in particular JV 85;

C12 photosynthesis inhibitors:

- pyridate or pyridafol, in particular pyridate;
- benzothiadiazinones, in particular bentazone;
- dipyridylenes, in particular paraquat-dichloride;
- ureas, in particular diuron or isoproturon, preferably diuron;
- phenols, in particular bromoxynil;
- chloridazone;
- triazines, in particular atrazine or terbutylazine; or
- triazinones, in particular metribuzin;

30

C13 synergists:

- oxiranes, in particular tridiphane;

C14 growth substances:

- aryloxyalkanoic acids, in particular fluoroxypry, MCPA or mecoprop-P;
- benzoic acids, in particular dicamba; or
- quinolinecarboxylic acids, in particular quinolac;

C16 various other herbicides:

- triaziflam.

5 In particular, compounds from amongst the classes of active ingredients mentioned below are preferred, or the following compounds are very particularly preferred.

C9 lipid biosynthesis inhibitors:

10

- chloroacetanilides, in particular dimethenamid, S-dimethenamid, acetochlor, metolachlor or S-metolachlor;

C12 photosynthesis inhibitors:

15

- pyridate;
- benzothiadiazinones, in particular bentazone;
- dipyridylenes, in particular paraquat-dichloride;
- ureas, in particular diuron or isoproturon, preferably diuron;
- phenols, in particular bromoxynil;
- chloridazon;
- triazines, in particular atrazine or terbutylazine; or
- triazinones, in particular metribuzin;

20

25

For particular preferred embodiments, the respective preferences described above apply analogously.

Especially preferred are synergistic herbicidal mixtures which 30 comprise as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B two herbicides selected from the group including imazapyr, imazaquin, imazamethabenz-methyl, imazamox, imazapic and imazetapyr, in particular imazapyr and imazetapyr or 35 imazetapyr and imazapic; and as component C a herbicidal compound from the group C9, in particular a chloroacetanilide, especially acetochlor.

In particular preferred are synergistic herbicidal mixtures which comprise as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B imazapyr and imazetapyr; and as component C a chloroacetanilide, especially acetochlor.

In particular preferred are synergistic herbicidal mixtures which comprise as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B imazapyr and imazapic; and as component C a chloroacetanilide, especially acetochlor.

Also especially preferred are synergistic herbicidal mixtures which comprise as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B two herbicides selected from the group including imazapyr, imazaquin, imazamethabenz-methyl, imazamox, imazapic and imazetapyr, in particular imazapyr and imazetapyr or imazapyr and imazapic; and as component C a herbicidal compound from the group C12, in particular a triazine, especially atrazine, or a benzothiadiazinone, especially bentazone.

In particular preferred are synergistic herbicidal mixtures which comprise as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B imazapyr and imazetapyr; and as component C a triazine, especially atrazine.

Also in particular preferred are synergistic herbicidal mixtures which comprise as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B imazapyr and imazetapyr; and as component C a benzothiadiazinone, especially bentazone.

Also in particular preferred are synergistic herbicidal mixtures which comprise as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B imazapyr and imazapic; and as component C a triazine, especially atrazine.

Also in particular preferred are synergistic herbicidal mixtures which comprise as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B imazapyr and imazapic; and as component C a benzothiadiazinone, especially bentazone.

The present invention also extends to herbicidal compositions which comprise a herbicidally active amount of a synergistic herbicidal mixture (comprising components A), B) and, if desired, C) as described above), at least one liquid and/or solid carrier and, if desired, at least one surfactant.

The herbicidal compositions and synergistic herbicidal mixtures according to the invention can effect very good control of broad-leaved weeds and grass weeds in crops such as maize, cereals, rice and soya without damaging the crop plants, an effect observed especially even at low rates of application.

Taking into consideration the variety of application method in question, the herbicidal compositions and synergistic herbicidal mixtures according to the invention can additionally be employed in a further number of crop plants for eliminating undesirable plants. Examples of suitable crops are the following:

Allium cepa, Ananas comosus, Arachis hypogaea, Asparagus officinalis, Beta vulgaris ssp. altissima, Beta vulgaris ssp. rapa, Brassica napus var. napus, Brassica napus var. napobrassica, Brassica rapa var. silvestris, Camellia sinensis, Carthamus tinctorius, Carya illinoiensis, Citrus limon, Citrus sinensis, Coffea arabica (Coffea canephora, Coffea liberica), Cucumis sativus, Cynodon dactylon, Daucus carota, Elaeis guineensis, Fragaria vesca, Glycine max, Gossypium hirsutum, (Gossypium arboreum, Gossypium herbaceum, Gossypium vitifolium), Helianthus annuus, Hevea brasiliensis, Hordeum vulgare, Humulus lupulus, Ipomoea batatas, Juglans regia, Lens culinaris, Linum usitatissimum, Lycopersicon lycopersicum, Malus spp., Manihot esculenta, Medicago sativa, Musa spp., Nicotiana tabacum (N.rustica), Olea europaea, Oryza sativa, Phaseolus lunatus, Phaseolus vulgaris, Picea abies, Pinus spp., Pisum sativum, Prunus avium, Prunus

persica, Pyrus communis, Ribes sylvestre, Ricinus communis, Saccharum officinarum, Secale cereale, Solanum tuberosum, Sorghum bicolor (s. vulgare), Theobroma cacao, Trifolium pratense, Triticum aestivum, Triticum durum, Vicia faba, Vitis vinifera und 5 Zea mays.

Moreover, the herbicidal compositions and synergistic herbicidal mixtures according to the invention can also be used in crops which tolerate the action of herbicides due to breeding, includ- 10 ing genetic engineering methods.

The mixtures according to the invention, or the herbicidal compositions comprising them, can be employed, for example, in the form of directly sprayable aqueous solutions, powders, suspen- 15 sions, also highly-concentrated aqueous, oily or other suspen- sions or dispersions, emulsions, oil dispersions, pastes, dusts, materials for spreading or granules, by means of spraying, atom- izing, dusting, spreading or pouring.

20 The use forms depend on the intended purposes; in any case, they should guarantee the finest possible distribution of the active ingredients according to the invention.

Suitable inert auxiliaries are mineral oil fractions of medium 25 to high boiling point such as kerosene and diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, e.g. paraffins, tetrahydronaphthalene, alkylated naphthalenes and their derivatives, alkylated benzenes and their derivatives, alcohols such as 30 methanol, ethanol, propanol, butanol and cyclohexanol, ketones such as cyclohexanone, strongly polar solvents, such as N-methylpyrrolidone and water.

Aqueous use forms can be prepared from emulsion concentrates, 35 suspensions, pastes, wettable powders or water-dispersible granules by adding water. To prepare emulsions, pastes or oil dispersions, the substances, as such or dissolved in an oil or solvent, can be homogenized in water by means of wetting agent, tackifier, dispersant or emulsifier. However, it is also possi-

ble to prepare concentrates composed of active substance, wetting agent, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and these concentrates are suitable for dilution with water.

5

Suitable surfactants are the alkali metal, alkaline earth metal and ammonium salts of aromatic sulfonic acids, e.g. ligno-, phenol-, naphthalene- and dibutylnaphthalenesulfonic acid, and of fatty acids, of alkyl- and alkylaryl sulfonates, of alkyl sulfates, lauryl ether sulfates and fatty alcohol sulfates, and salts of sulfated hexa-, hepta- and octadecanols, and of fatty alcohol glycol ether, condensates of sulfonated naphthalene and its derivatives with formaldehyde, condensates of naphthalene, or of the naphthalenesulfonic acids, with phenol and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated iso-octyl-, octyl- or nonylphenol, alkylphenyl and tributylphenyl polyglycol ether, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene alkyl ethers, lauryl alcohol polyglycol ether acetate, sorbitol esters, lignin-sulfite waste liquors or methylcellulose.

Powders, materials for spreading and dusts can be prepared by mixing or concomitantly grinding the synergistic herbicidal mixture or the individual active ingredients with a solid carrier.

Granules, e.g. coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active ingredients to solid carriers. Solid carriers are mineral earths such as silicas, silica gels, silicates, talc, kaolin, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic material, fertilizers such as ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas and products of vegetable origin such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders or other solid carriers.

The concentrations of the mixtures according to the invention in the ready-to-use products can be varied within wide ranges. In

general, the formulations comprise from 0.01 to 95% by weight, preferably 0.5 to 90% by weight, of the mixture according to the invention.

5 The components A) and B) and, if desired, C) can be formulated jointly, but also separately, and/or applied to the plants, their environment and/or seeds jointly or separately. It is preferable to apply the active ingredients simultaneously. However, it is also possible to apply them separately.

10 Also the two herbicides of component B) can be formulated separately, and/or applied to the plants, their environment and/or seeds jointly or separately.

15 Moreover, it may be advantageous to apply the herbicidal compositions and synergistic herbicidal mixtures according to the invention, jointly or separately, with additional other crop protection agents, for example with pesticides or agents for controlling phytopathogenic fungi or bacteria. Also of interest is 20 the miscibility with mineral salt solutions which are employed for treating nutritional and trace element deficiencies. Non-phytotoxic oils and oil concentrates can also be added.

25 The mixtures according to the invention and the herbicidal compositions can be applied pre- or post-emergence. If the active ingredients are less well tolerated by certain crop plants, application techniques may be used in which the herbicidal compositions are sprayed, with the aid of the spray apparatus, in such a way that they come into as little contact, if any, with 30 the leaves of the sensitive crop plants while reaching the leaves of undesirable plants which grow underneath, or the bare soil (post-directed, lay-by).

35 In the case of a post-emergence treatment of the plants, the herbicidal compositions according to the invention are preferably applied by foliar application. Application may be effected, for example, by usual spraying techniques with water as the carrier, using amounts of spray mixture of approx. 100 to 1000 l/ha. The compositions may also be applied by the so-called

"low-volume" and "ultra-low-volume" methods, or in the form of so-called granules.

As a rule, the synergistic herbicidal mixtures comprise components 5 A), B) and, if desired, C) in such weight ratios that the synergistic effect takes place.

The ratios of component A) and B) in the mixture preferably range from 1:0.001 to 1:500, preferably from 1:0.01 to 1:100, particularly preferably from 1:0.1 to 1:50.

10 The ratios of components A) and C) in the mixture preferably range from 1:0.002 to 1:800, preferably from 1:0.003 to 1:250, especially from 1:0.003 to 1:160, particularly preferably from 1:0.02 to 1:250, especially particularly preferably from 1:0.02 to 1:160.

15 The rate of application of pure synergistic herbicidal mixture, i.e. without formulation auxiliaries, amounts to 0.2 to 5000 g/ha, especially to 1 to 2000 g/ha, preferably to 2 to 2000 g/ha, in particular to 8 to 1500 g/ha, of active substance 20 (a.s.), depending on the intended aim, the season, the target plants and growth stage.

The rate of application of 3-heterocyclyl-substituted benzoyl derivative of the formula I is 0.1 to 250 g/ha, as a rule 0.5 to 25 250 g/ha, especially 5 to 250 g/ha, preferably 10 to 150 g/ha, of active substance (a.s.).

The preferred rate of application of component B) is 0.1 to 250 g/ha, as a rule 0.5 to 120 g/ha, especially 1 to 120 g/ha, preferably 30 10 to 100 g/ha, of active substance (a.s.).

The preferred application rate of the active ingredients of the optional component C) are compiled in Table 2.

Table 2

Component C	Class of active ingredient	Active ingredient (g/ha)	Rate of application (g/ha)
C1 acetyl-CoA carboxylase inhibitors	cyclohexenone oxime ethers		25-400
		cycloxydim	100-400
		sethoxydim	100-400
		tralkoxydim	100-400
	phenoxyphenoxypropionic esters		25-300
		clodinafpop-P-propargyl ^a	25-100
		fenoxaprop-ethyl	50-300
		fenoxaprop-P-ethyl	25-150
C2 acetolactate synthase inhibitors (ALS)	imidazolinones		0.2-800
		imazapyr	0.2-800
		imazaquin	0.3-400
		imazamethabenz	0.5-300
		imazapic	1-800
		imazethapyr	0.2-400
		imazamox	0.3-150
	pyrimidyl ethers		0.2-120
		pyrithiobac-sodium	2-120
	sulfonamides		1-225
		florasulam	1-20

	flumetsulam	25-225
	metosulam	1-60
	halosulfuron-methyl	5-120
	nicosulfuron	1-120
	primisulfuron-methyl	10-120
	prosulfuron	10-120
	rim sulfuron	5-120
	thifensulfuron-methyl	10-60
	tribenuron-methyl	10-60
	N-[[[4-methoxy-6-(trifluoromethyl)-1,3,5-triazin-2-yl]amino]-carbonyl]-2-(trifluoromethyl)-benzenesulfonamide	5-120
	sulfosulfuron	10-60
C3 amides		250-2000
	fluthianide	250-2000
C4 auxin herbicides		25-750
	pyridinecarboxylic acids	25-750
	clopyralid	25-750
	2,4-D	50-750
C5 auxin transport inhibitors		15-100
	diflufenzopyr	15-100
C6 carotenoid biosynthesis inhibitors		25-600
	isoxaflutole	25-200

		sulcotrione	100-600
	-	mesotrione	25-300
	-	isoxachlortole	25-200
	-	ketospiradox	25-300
C7	enolpyruvylshikimat-3-phosphate synthase inhibitors (EPSPS)		360-1080
	-	glyphosate	360-1080
	-	sulfosate	360-1080
C8	glutamine synthetase inhibitors		10-600
	-	glufosinate-ammonium	10-600
C9	lipid biosynthesis inhibitors		60-4000
	-	chloroacetanilides	60-2000
		dimethenamid	60-2000
		S-dimethenamid	60-2000
		acetochlor	250-4000
		metolachlor	60-4000
		S-metolachlor	60-4000
		thioureas	100-4000
C10	mitosis inhibitors		1000-4000
		benthiocarb	375-3000
		dinitroanilines	375-3000
C11	protoporphyrinogen IX oxidase inhibitors		375-3000
		pendimethalin	0.5-600
		diphenyl ethers	50-300

	acifluorfen	50-300
	acifluorfen-sodium	50-300
		50-600
oxadiazoles	oxadiargyl	50-600
cyclic imides		0.5-300
	carfentrazone-ethyl	0.5-35
	cinidon-ethyl	3-35
	flumiclorac-pentyl	3-35
	butafenacil	5-300
	JV 485	50-300
C12 photosynthesis inhibitors		15-4000
	pyridate	250-1500
	pyridafol	250-1000
	benzothiadiazinones	30-1440
	bentazone	30-1440
	dipyridylenes	100-800
	paraquat-dichloride	100-800
	ureas	250-1600
	diuron	250-1600
	isoproturon	250-1600
	phenols	100-700
	bromoxynil	100-700
	chlordazon	500-4000
	triazines	15-4000
	atrazine	15-4000

		terbutylazine	250-4000
	triazimone		30-300
		metribuzin	30-300
C13 synergists			500-1500
	oxiranes		500-1500
		tridiphane	500-1500
C14 growth substances			25-1200
	aryloxyalkanoic acids		50-1200
		fluoroxypryr	50-400
		MCPA	400-1200
		mecoprop-P	400-1200
	benzoic acids		75-800
		dicamba	75-800
	quinolinicarboxylic acids		25-600
C16 various other herbicides		quinclorac	25-600
		triaziflam	50-750
		-	

^a If appropriate, 10-50 g/ha cloquintocet may also be added.

Use examples

5 The mixtures according to the invention were applied pre- or post-emergence (foliar treatment). The herbicidal compounds of component B and, if desired, of component C were applied in the formulation in which they are present as commercially available product.

10 The herbicidally active compounds of components A), B) and, if desired, C) were applied in succession or jointly, in the latter case in some cases as a tank mix and in some cases as a ready-mix, in the form of emulsions, aqueous solutions or suspensions, the vehicle being water (300 - 400 l/ha). In the case of the field trials, application was effected with the aid of a mobile 15 plot sprayer.

The test period extended over 3 to 8 weeks, and the stands were also observed at later points in time.

20 Damage by the herbicidal compositions was evaluated with reference to a scale of 0% to 100% in comparison with untreated control plots. 0 means no damage and 100 means complete destruction of the plants.

25 The following examples will demonstrate the action of the herbicidal compositions which can be used according to the invention, without excluding the possibility of other uses.

30 In these examples, the value E at which only an additive effect of the individual active ingredients is to be expected was calculated by the method of S. R. Colby (Calculating synergistic and antagonistic responses of herbicide combinations, Weeds 15, 20 pp (1967)).

35 This was done using the formula

$$E = X + Y - \frac{XY}{100}$$

where

X = Percentage of the herbicidal action of X at an application
5 rate of x;

Y = Percentage of the herbicidal action of Y at an application
rate of Y;

10 E = expected herbicidal action of X + Y at rates of application
x + y (in %);

or the formula

$$E = X + Y + Z - \frac{(XY + XZ + YZ)}{100} + \frac{XYZ}{10000}$$

15

where

X = Percentage of the herbicidal action of X at an application
20 rate of x;

Y = Percentage of the herbicidal action of Y at an application
rate of y;

25 Z = Percentage of the herbicidal action of Z at an application
rate of Z;

E = expected herbicidal action of X + Y + Z at rates of applica-
tion x + y + z (in %).

30

If the value observed exceeds the value E calculated in accord-
ance with Colby's formula, then synergism is present.

35 The herbicidal mixtures according to the invention exert a
greater herbicidal action than would have been expected accord-
ing to Colby on the basis of the observed effects of the indi-
vidual components when used alone.

The results of the tests are shown in Tables 3 to 17 below.

In these studies, the following plants were used:

5

Scientific name	Common name
<i>Abutilon theophrasti</i>	Velvetleaf
<i>Amaranthus retroflexus</i>	Pigweed
<i>Avena fatua</i>	Wild oat
<i>Brachiaria plantaginea</i>	Alexandergrass
<i>Commelina benghalensis</i>	Bengal commelina
<i>Echinochloa crus-galli</i>	Barnyardgrass
<i>Galium aparine</i>	Catchweed
<i>Pharbitis purpurea</i>	Common morningglory
<i>Polygonum persicaria</i>	Ladysthumb

10 Table 3: Herbicidal action of compound 1a.29 and imazapyr and imazethapyr¹ (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Abutilon theophrasti	Colby Value
		Damage [%]	E
Ia.29	0.98	30	-
imazapyr +	0.98	20	-
imazethapyr			
Ia.29 + imazapyr + imazethapyr	0.98	55	44

Table 4: Herbicidal action of compound 1a.29 and imazapyr and imazethapyr¹ (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Commelina benghalensis	Colby Value
		Damage [%]	E
Ia.29	3.91	50	-
imazapyr +	3.91	10	-
imazethapyr			
Ia.29 +	3.91		
imazapyr +	3.91	70	55
imazethapyr			

5

Table 5: Herbicidal action of compound 1a.29 and imazapic and imazapyr² (post-emergence treatment; greenhouse)

10

	Application rate [g/ha ai]	Avena fatua	Colby Value E	Amaranthus retroflexus	Colby Value E
		Damage [%]		Damage [%]	
Ia.29	0.98	0	-	60	-
imazapic +	0.98	10	-	20	-
imazapyr					
Ia.29 +	0.98				
imazapic +	0.98	40	10	75	68
imazapyr					

Table 6: Herbicidal action of compound 1a.29 and imazapic and imazapyr² (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Avena fatua	Colby Value E
		Damage [%]	
Ia.29	1.95	10	-
imazapic + imazapyr	1.95	25	-
Ia.29 + imazapic + imazapyr	1.95	60	33

5

Table 7: Herbicidal action of compound 1a.29, imazapyr and imazethapyr¹, and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Amaranthus retroflexus	Colby Value E	Gallium aparine	Colby Value E
		Damage [%]		Damage [%]	
Ia.29	0.98	60	-	20	-
imazapyr + imazethapyr	0.98	20	-	20	-
atrazine	15.6	40	-	0	-
Ia.29 + imazapyr + imazethapyr + atrazine	0.98 + 0.98 + 15.6	85	81	50	36

Table 8: Herbicidal action of compound 1a.29, imazapyr and imazethapyr¹, and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Galium aparine	Colby Value E
		Damage [%]	
Ia.29	1.95	30	-
imazapyr			
+	1.95	40	-
imazethapyr			
atrazine	31.25	20	-
Ia.29	1.95		
+	+		
imazapyr			
+	1.95	70	66
imazethapyr			
+	+		
atrazine	31.25		

5

Table 9: Herbicidal action of compound 1a.29, imazapic and imazapyr², and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Abutilon theophrasti	Colby Value E
		Damage [%]	
Ia.29	7.81	85	-
imazapic			
+	7.81	70	-
imazapyr			
atrazine	125	30	-
Ia.29	7.81		
+	+		

imazapic + imazapyr + atrazine	7.81 + 125	100	97
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5 Table 10: Herbicidal action of compound 1a.29, imazapyr and imazethapyr¹, and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Brachiaria plantaginea	Colby	Echinochloa crus-galli	Colby
		Damage [%]	E	Damage [%]	E
Ia.29 + imazapyr + imazethapyr	7.81 + 7.81	85	-	80	-
Atrazine	125	25	-	30	
Ia.29 + imazapyr + imazethapyr + atrazine	7.81 + 7.81 + 125	100	89	100	86

Table 11: Herbicidal action of compound 1a.29, imazapyr and imazethapyr¹, and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Galium aparine	Colby Value E	Polygonum persicaria	Colby Value E
		Damage [%]		Damage [%]	
Ia.29	7.81				
+	+				
imazapyr		70	-	75	-
+	7.81				
imazethapyr					
atrazine	125	60	-	60	
Ia.29	7.81				
+	+				
imazapyr		98	88	100	90
+	7.81				
imazethapyr					
+	+				
atrazine	125				

5

10 Table 12: Herbicidal action of compound 1a.29, imazapyr and imazethapyr¹, and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Echinochloa crus-galli	Colby Value E	Pharbitis purpurea	Colby Value E
		Damage [%]		Damage [%]	
Ia.29	3.91				
+	+				
imazapyr		85	-	50	-
+	3.91				
imazethapyr					
atrazine	62.5	20	-	80	

Ia.29	3.91				
+	+				
imazapyr					
+	3.91	95	88	100	90
imazethapyr					
+	+				
atrazine	62.5				

5 Table 13: Herbicidal action of compound Ia.29, imazapyr and imazethapyr¹, and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Polygonum persicaria	Colby Value E
		Damage [%]	
Ia.29	3.91		
+	+		
imazapyr		70	-
+	3.91		
imazethapyr			
atrazine	62.5	40	
Ia.29	3.91		
+	+		
imazapyr			
+	3.91	100	82
imazethapyr			
+	+		
atrazine	62.5		

Table 14: Herbicidal action of compound 1a.29, imazapic and imazapyr², and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Echinochloa crus-galli	Colby	Abutilon theophrasti	Colby
		Damage [%]	E	Damage [%]	Value E
Ia.29	7.81				
+	+				
imazapic		80	-	85	-
+	7.81				
imazapyr					
atrazine	125	30	-	30	
Ia.29	7.81				
+	+				
imazapic		100	86	100	90
+	7.81				
imazapyr					
+	+				
atrazine	125				

5

10 Table 15: Herbicidal action of compound 1a.29, imazapic and imazapyr², and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Galium aparine	Colby
		Damage [%]	Value E
Ia.29	7.81		
+	+		
imazapic		80	-
+	7.81		
imazapyr			
atrazine	125	60	

Ia.29	7.81		
+	+		
imazapic			
+	7.81	98	92
imazapyr			
+	+		
atrazine	125		

5 Table 16: Herbicidal action of compound Ia.29, imazapic and imazapyr², and atrazine (post-emergence treatment; greenhouse).

	Application rate [g/ha ai]	Brachiaria plantaginea	Colby Value E	Echinochloa crus-galli	Colby Value E
		Damage [%]		Damage [%]	
Ia.29	3.91				
+	+				
imazapic					
+	3.91	85	-	80	-
imazapyr					
atrazine	62.5	20	-	20	
Ia.29	3.91				
+	+				
imazapic					
+	3.91	100	88	98	84
imazapyr					
+	+				
atrazine	62.5				

Table 17: Herbicidal action of compound Ia.29, imazapic and imazapyr², and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Polygonum persicaria	Colby Value E
		Damage [%]	
Ia.29 + imazapic + imazapyr	3.91 + 3.91	70	-
atrazine	62.5	40	
Ia.29 + imazapic + imazapyr + atrazine	3.91 + 3.91 + 62.5	100	82

5

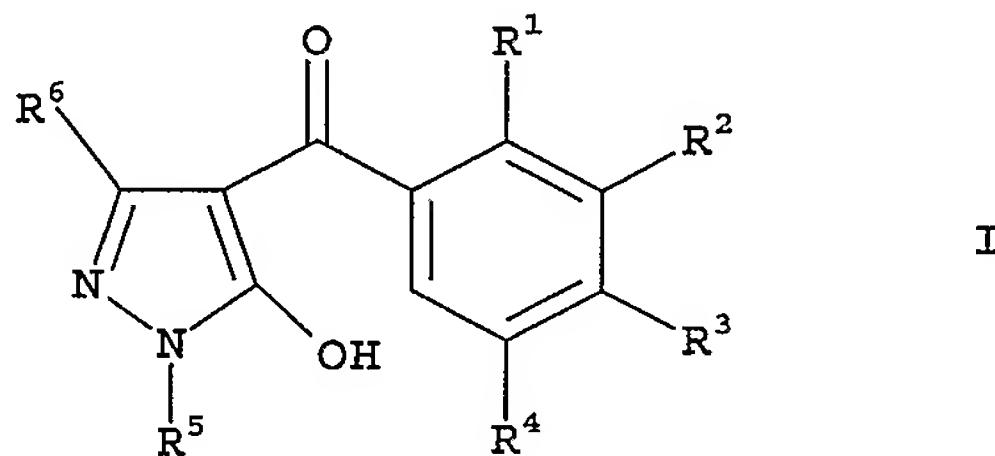
¹ imazapyr : imazethapyr = 1 : 3

² imazapic : imazapyr = 3 : 1

We claim:

1. A synergistic herbicidal mixture comprising

5 A) at least one 3-heterocyclyl-substituted benzoyl derivative of the formula I



10 in which the variables have the following meanings:

R^1 , R^3 are halogen, C_1-C_6 -alkyl, C_1-C_6 -haloalkyl, C_1-C_6 -alkoxy, C_1-C_6 -haloalkoxy, C_1-C_6 -alkylthio, C_1-C_6 -alkylsulfinyl or C_1-C_6 -alkylsulfonyl;

15 R^2 is a heterocyclic radical selected from the group: isoxazol-3-yl, isoxazol-4-yl, isoxazol-5-yl, 4,5-dihydroisoxazol-3-yl, 4,5-dihydroisoxazol-4-yl and 4,5-dihydroisoxazol-5-yl, it being possible for the six radicals mentioned to be unsubstituted or mono- or polysubstituted by halogen, C_1-C_4 -alkyl, C_1-C_4 -alkoxy, C_1-C_4 -haloalkyl, C_1-C_4 -haloalkoxy or C_1-C_4 -alkylthio;

20 R^4 is hydrogen, halogen or C_1-C_6 -alkyl;

R^5 is C_1-C_6 -alkyl;

R^6 is hydrogen or C_1-C_6 -alkyl;

25 or one of its environmentally compatible salts;

30 and

B) two herbicides selected from the group including imazapyr, imazaquin, imazamethabenz-methyl, imazamox, imazapic and imazethapyr;

5 or one of its environmentally compatible salts;

and, if desired,

10 C) at least one herbicidal compound from the group of the acetyl-CoA carboxylase inhibitors (ACC), acetolactate synthase inhibitors (ALS), amides, auxin herbicides, auxin transport inhibitors, carotenoid biosynthesis inhibitors, enolpyruvylshikimate 3-phosphate synthase inhibitors (EPSPS), glutamine synthetase inhibitors, 15 lipid biosynthesis inhibitors, mitosis inhibitors, protoporphyrinogen IX oxidase inhibitors, photosynthesis inhibitors, synergists, growth substances, cell wall biosynthesis inhibitors and a variety of other herbicides;

20 in a synergistically effective amount.

2. A synergistic herbicidal mixture as claimed in claims 1, 25 comprising, as component A), a 3-heterocyclyl-substituted benzoyl derivative of the formula I, where R⁴ is hydrogen.

3. A synergistic herbicidal mixture as claimed in any of claims 1 to 2, comprising, as component A), a 3-heterocyclyl- 30 substituted benzoyl derivative of the formula I, where

R¹ is halogen, C₁-C₆-alkyl or C₁-C₆-alkylsulfonyl;

R³ is halogen or C₁-C₆-alkylsulfonyl;

35 4. A synergistic herbicidal mixture as claimed in any of claims 1 to 3, comprising, as component A), a 3-heterocyclyl-substituted benzoyl derivative of the formula I, where

R² is a heterocyclic radical selected from the group: isoxazol-3-yl, isoxazol-5-yl and 4,5-dihydroisoxazol-3-yl, it being possible for the three radicals mentioned to be unsubstituted or mono- or polysubstituted by halogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkyl, C₁-C₄-haloalkoxy or C₁-C₄-alkylthio.

5. A synergistic herbicidal mixture as claimed in any of claims 1 to 4, comprising, as component A), a 3-heterocyclyl-substituted benzoyl derivative of the formula I, where

R² is isoxazol-5-yl, 3-methyl-isoxazol-5-yl, 4,5-dihydroisoxazol-3-yl, 5-methyl-4,5-dihydroisoxazol-3-yl, 5-ethyl-4,5-dihydroisoxazol-3-yl or 4,5-dimethyl-4,5-dihydroisoxazol-3-yl.

6. A synergistic herbicidal mixture as claimed in any of claims 1 to 5, comprising, as component A), 4-[2-chloro-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole.

7. A synergistic herbicidal mixture as claimed in any of claims 1 to 5, comprising, as component A) 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole.

8. A synergistic herbicidal mixture as claimed in any of claims 1 to 7, comprising as component B) imazapyr and imazethapyr.

30 9. A synergistic herbicidal mixture as claimed in any of claims 1 to 7, comprising as component B) imazapic and imazapyr.

10. A synergistic herbicidal mixture as claimed in any of claims 1 to 7, comprising, three active ingredients, a 3-heterocyclyl-substituted benzoyl derivative of the formula I (component A) as claimed in claims 1 to 7 and imazapyr and imazethapyr (component B).

11. A synergistic herbicidal mixture as claimed in any of claims 1 to 7, comprising, three active ingredients, a 3-heterocyclyl-substituted benzoyl derivative of the formula I (component A) as claimed in claims 1 to 7 and imazapic and 5 imazapyr (component B).

12. A synergistic herbicidal mixture as claimed in any of claims 1 to 7, comprising, at least four active ingredients, a 3-heterocyclyl-substituted benzoyl derivative of the formula I (component A) as claimed in claims 1 to 7; 10 two herbicides selected from the group including imazapyr, imazaquin, imazamethabenz-methyl, imazamox, imazapic and imazethapyr (component B) as claimed in claims 1;

15 and

20 C) at least one herbicidal compound from the group of the acetyl-CoA carboxylase inhibitors (ACC), acetolactate synthase inhibitors (ALS), amides, auxin herbicides, auxin transport inhibitors, carotenoid biosynthesis inhibitors, enolpyruvylshikimate 3-phosphate synthase inhibitors (EPSPS), glutamine synthetase inhibitors, lipid biosynthesis inhibitors, mitosis inhibitors, protoporphyrinogen IX oxidase inhibitors, photosynthesis 25 inhibitors, synergists, growth substances, cell wall biosynthesis inhibitors and a variety of other herbicides.

30 13. A synergistic herbicidal mixture as claimed in claim 1 or 12 comprising, as component C), at least one herbicidal compound from the groups C1 to C16:

35 C1 acetyl-CoA carboxylase inhibitors (ACC): cyclohexenone oxime ethers, phenoxyphenoxypropionic esters or arylaminopropionic acids;

C2 acetolactate synthase inhibitors (ALS): imidazolinones, pyrimidyl ethers, sulfonamides or sulfonylureas;

C3 amides;

5 C4 auxin herbicides:
pyridinecarboxylic acids, 2,4-D or benazolin;

10 C5 auxin transport inhibitors;

C6 carotenoid biosynthesis inhibitors;

15 C7 enolpyruvylshikimate 3-phosphate synthase inhibitors
(EPSPS);

C8 glutamine synthetase inhibitors;

20 C9 lipid biosynthesis inhibitors:
anilides, chloroacetanilides, thioureas, benfuresate or
perfluidone;

C10 mitosis inhibitors:
carbamates, dinitroanilines, pyridines, butamifos,
chlorthal-dimethyl (DCPA) or maleic hydrazide;

25 C11 protoporphyrinogen IX oxidase inhibitors:
diphenyl ethers, oxadiazoles, cyclic imides or pyra-
zoles;

30 C12 photosynthesis inhibitors:
propanil, pyridate, pyridafol, benzothiadiazinones, di-
nitrophenols, dipyridylenes, ureas, phenols, chlorida-
zon, triazines, triazinones, uracils or biscarbamates;

35 C13 synergists:
oxiranes;

C14 growth substances:
aryloxyalkanoic acids, benzoic acids or quinolinecar-
boxylic acids;

C15 cell wall synthesis inhibitors:

C16 various other herbicides:

5 dichloropropionic acids, dihydrobenzofurans, phenylactic acids or aziprotryn, barban, bensulide, benzthiazuron, benzofluor, buminafos, buthidazole, buturon, 10 cafenstrole, chlorbufam, chlorofenprop-methyl, chloroxuron, cinmethylin, cumyluron, cycluron, cyprazine, cyprazole, dibenzyluron, dipropetryn, dymron, egliazin-ethyl, endothall, ethiozin, flucabazole, fluorbentranil, flupoxam, isocarbamid, isopropalin, karbutilate, mefluidide, monuron, napropamide, napropanilide, nitralin, oxaciclomefone, phenisopham, piperophos, procyzine, profluralin, pyributicarb, secbumeton, sulfalate 15 (CDEC), terbucarb, triazofenamide, triaziflam or trimeturon;

or their environmentally compatible salts.

20 14. A synergistic herbicidal mixture as claimed in claims 1 or 12, comprising, as component C), at least one herbicidal compound from the groups C1 to C16:

C1 acetyl-CoA carboxylase inhibitors (ACC) :

25 - cyclohexenone oxime ethers:
alloxydim, clethodim, cloproxydim, cycloxydim,
sethoxydim, tralkoxydim, butroxydim, clefoxydim or
tepraloxoxydim;

30 - phenoxyphenoxypropionic esters:
clodinafop-propargyl (and, if appropriate, clo-
quintocet), cyhalofop-butyl, diclofop-methyl,
fenoxaprop-ethyl, fenoxaprop-P-ethyl, fen-
thiapropropethyl, fluazifop-butyl, fluazifop-P-butyl,
haloxyfop-ethoxyethyl, haloxyfop-methyl, haloxy-
fop-P-methyl, isoxapryifop, propaquizafop, qui-
zalofop-ethyl, quizalofop-P-ethyl or quizalofop-
tefuryl; or

35 - arylaminopropionic acids:
flamprop-methyl or flamprop-isopropyl;

C2 acetolactate synthase inhibitors (ALS):

- imidazolinones:
imazapyr, imazaquin, imazamethabenz-methyl, imazamox, imazapic or imazethapyr;
- pyrimidyl ethers:
pyrithiobac-acid, pyrithiobac-sodium, bispyribac-sodium, KIH-6127 or pyribenzoxym;
- sulfonamides:
florasulam, flumetsulam or metosulam; or
- sulfonylureas:
amidosulfuron, azimsulfuron, bensulfuron-methyl, chlorimuron-ethyl, chlorsulfuron, cinosulfuron, cyclosulfamuron, ethametsulfuron-methyl, ethoxy-sulfuron, flazasulfuron, halosulfuron-methyl, imazosulfuron, metsulfuron-methyl, nicosulfuron, primisulfuron-methyl, prosulfuron, pyrazosulfuron-ethyl, rimsulfuron, sulfometuron-methyl, thifensulfuron-methyl, triasulfuron, tribenuron-methyl, triflusulfuron-methyl, N-[[[4-methoxy-6-(trifluoromethyl)-1,3,5-triazin-2-yl]amino]-carbonyl]-2-(trifluoromethyl)-benzenesulfonamide, sulfosulfuron or iodosulfuron;

25 C3 amides:

- allidochlor (CDAA), benzoylprop-ethyl, bromobutide, chlorthiamid, diphenamid, etobenzanid (benzchlomet), fluthiamide, fosamin or monalide;

30 C4 auxin herbicides:

- pyridine carboxylic acids:
clopyralid or picloram; or
- 2,4-D or benazolin;

35 C5 auxin transport inhibitors:

- naptalame or diflufenzopyr;

C6 carotenoid biosynthesis inhibitors:

- benzofenap, clomazone (dimethazone), diflufenican, fluorochloridone, fluridone, pyrazolynate, pyrazoxyfen, isoxaflutole, isoxachlortole, mesotrione, sulcotrione (chlormesulone), ketospiradox, flurtamone, norflurazon or amitrol;

5

C7 enolpyruvylshikimate-3-phosphate synthase inhibitors (EPSPS):

- glyphosate or sulfosate;

10

C8 glutamine synthetase inhibitors:

- bilanafos (bialaphos) or glufosinate-ammonium;

C9 lipid biosynthesis inhibitors:

- anilides:

anilofos or mefenacet;

- chloroacetanilides:

dimethenamid, S-dimethenamid, acetochlor, alachlor, butachlor, butenachlor, diethyl-ethyl, dimethachlor, metazachlor, metolachlor, S-metolachlor, pretilachlor, propachlor, prynachlor, terbuchlor, thenylchlor or xylachlor;

- thioureas:

butylate, cycloate, di-allate, dimepiperate, EPTC, esprocarb, molinate, pebulate, prosulfocarb, thiobencarb (benthiocarb), tri-allate or vernolate; or

- benfuresate or perfluidone;

20

25

C10 mitosis inhibitors:

- carbamates:

asulam, carbetamid, chlorpropham, orbencarb, pronamid (propyzamid), propham or tiocarbazil;

- dinitroanilines:

benefin, butralin, dinitramin, ethalfluralin, fluchloralin, oryzalin, pendimethalin, prodiamine or trifluralin;

- pyridines:

dithiopyr or thiazopyr; or

30

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- butamifos, chlorthal-dimethyl (DCPA) or maleic hydrazide;

5 C11 protoporphyrinogen IX oxidase inhibitors:

- diphenyl ethers:
acifluorfen, acifluorfen-sodium, aclonifen, bifenox, chlornitrofen (CNP), ethoxyfen, fluorodifen, fluoroglycofen-ethyl, fomesafen, furyloxyfen, lactofen, nitrofen, nitrofluorfen or oxyfluorfen;
- oxadiazoles:
oxadiargyl or oxadiazon;
- cyclic imides:
azafenidin, butafenacil, carfentrazone-ethyl, cinidon-ethyl, flumiclorac-pentyl, flumioxazin, flumipropyn, flupropacil, fluthiacet-methyl, sulfentrazone or thidiazimin; or
- pyrazoles:
ET-751, JV 485 or nipyrapaclofen;

20 C12 photosynthesis inhibitors:

- propanil, pyridate or pyridafol;
- benzothiadiazinones:
bentazone;
- dinitrophenols:
bromofenoxim, dinoseb, dinoseb-acetate, dinoterb or DNOC;
- dipyridylenes:
cyperquat-chloride, difenzoquat-methylsulfate, diquat or paraquat-dichloride;
- ureas:
chlorbromuron, chlorotoluron, difenoxuron, dimefuron, diuron, ethidimuron, fenuron, fluometuron, isoproturon, isouron, linuron, methabenzthiazuron, methazole, metobenzuron, metoxuron, monolinuron, neburon, siduron or tebuthiuron;
- phenols:
bromoxynil or ioxynil;
- chloridazon;

- triazines:
ametryn, atrazine, cyanazine, desmetryn, di-methamethryne, hexazinone, prometon, prometryn, propazine, simazine, simetryn, terbumeton, ter-butryne, terbutylazine or trietazine;
- triazinones:
metamitron or metribuzine;
- uracils:
bromacil, lenacil or terbacil; or
- biscarbamates:
desmedipham or phenmedipham;

C13 synergists:

- oxiranes:
` tridiphane;

C14 growth substances:

- aryloxyalkanoic acids:
2,4-DB, clomeprop, dichlorprop, dichlorprop-P (2,4-DP-P), fluoroxypryn, MCPA, MCPB, mecoprop, mecoprop-P, or triclopyr;
- benzoic acids:
chloramben or dicamba; or
- quinolinecarboxylic acids:
quinclorac or quinmerac;

C15 cell wall synthesis inhibitors:

- isoxaben or dichlobenil;

C16 various other herbicides:

- dichloropropionic acids:
dalapon;
- dihydrobenzofurans:
ethofumesate;
- phenylacetic acids:
chlorfenac (fenac); or
- aziprotryne, barban, bensulide, benzthiazuron, benzofluor, buminafos, buthidazole, buturon, cafestrole, chlorbufam, chlorfenprop-methyl, chlo-

roxuron, cinmethylin, cumyluron, cycluron,
cyprazine, cyprazole, dibenzyluron, dipropetryn,
dymron, eglinazin-ethyl, endothall, ethiozin, flu-
cabazole, fluorbentranil, flupoxam, isocarbamid,
5 isopropalin, karbutilate, mefluidide, monuron,
napropamide, napropanilide, ntralin, oxaciclome-
fone, phenisopham, piperophos, procyzazine, proflu-
ralin, pyributicarb, secbumeton, sulfallate
(CDEC), terbucarb, triazofenamid, triaziflan or
10 trimeturon;

or their environmentally compatible salts.

15. A synergistic herbicidal mixture as claimed in 12, comprising,
15 as component C), at least one herbicidal compound from
the groups C9 or C12 as defined in claim 12.
16. A synergistic herbicidal mixture as claimed in claim 12
comprising, as component A) 4-[2-methyl-3-(4,5-dihydroisoxa-
20 zol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-
pyrazole; as component B) two herbicides selected from the
group including imazapyr, imazaquin, imazamethabenz-methyl,
imazamox, imazapic and imazethapyr; and as component C) a
herbicidal compound from the group C9.
25
17. A synergistic herbicidal mixture as claimed in claim 12
comprising, as component A) 4-[2-methyl-3-(4,5-dihydroisoxa-
zol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-
pyrazole, as component B) imazapyr and imazethapyr or imazapic
30 and imazapyr, and as component C) a chloroacetanilide.
18. A synergistic herbicidal mixture as claimed in claim 12 comprising,
as component A) 4-[2-methyl-3-(4,5-dihydroisoxa-
zol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-
pyrazole, as component B) imazapyr and imazethapyr as compo-
35 nent C) acetochlor.
19. A synergistic herbicidal mixture as claimed in claim 12 comprising,
as component A) 4-[2-methyl-3-(4,5-dihydroisoxa-

zol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole, as component B) imazapic and imazapyr, and as component C) acetochlor.

5 20. A synergistic herbicidal mixture as claimed in claim 12 comprising, as component A) 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B) two herbicides selected from the group including imazapyr, imazaquin, imazamethabenz-methyl, 10 imazamox, imazapic and imazethapyr; and as component C) a herbicidal compound from the group C12.

15 21. A synergistic herbicidal mixture as claimed in claim 12 comprising, as component A) 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole, as component B) imazapyr and imazethapyr, and as component C) a benzothiadiazine or a triazine.

20 22. A synergistic herbicidal mixture as claimed in claim 12 comprising, as component A) 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole, as component B) imazapyr and imazethapyr, and as component C) bentazone.

25 23. A synergistic herbicidal mixture as claimed in claim 12 comprising, as component A) 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole, as component B) imazapyr and imazethapyr as component C) atrazine.

30 24. A synergistic herbicidal mixture as claimed in claim 12 comprising, as component A) 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole, as component B) imazapic and imazapyr, and as component C) a benzothiadiazine or a triazine.

35 25. A synergistic herbicidal mixture as claimed in claim 12 comprising, as component A) 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-

pyrazole, as component B) imazapic and imazapyr, and as component C) bentazone.

26. A synergistic herbicidal mixture as claimed in claim 12
5 comprising, as component A) 4-[2-methyl-3-(4,5-dihydroisoxa-
zol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-
pyrazole, as component B) imazapic and imazapyr as component
C) atrazine.

10 27. Synergistic herbicidal mixture as claimed in any of claims 1
to 26, wherein component A) and B) are present in a weight
ratio of 1:0.001 to 1:500.

15 28. Synergistic herbicidal mixture as claimed in any of claims
12 to 26, wherein component A) and component C) are present
in a weight ratio of 1:0.002 to 1:800.

20 29. A herbicidal composition comprising a herbicidally active
amount of a synergistic herbicidal mixture as claimed in any
of claims 1 to 28, at least one inert liquid and/or solid
carrier and, if desired, at least one surfactant.

30 30. A process for the preparation of herbicidal compositions as
claimed in claim 29, wherein component A), component B), if
25 desired, component C), at least one inert liquid and/or
solid carrier and, if appropriate, a surfactant are mixed.

30 31. A method of controlling undesired vegetation, which com-
prises applying a synergistic herbicidal mixture as claimed
in any of claims 1 to 28 before, during and/or after the
emergence of undesired plants, it being possible for the
herbicidally active compounds of components A), B) and, if
desired, C) to be applied simultaneously or in succession.

35 32. A method of controlling undesired vegetation as claimed in
claim 31, wherein the leaves of the crop plants and of the
undesired plants are treated.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/07983A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A01N43/80

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 65314 A (BASF AG) 23 December 1999 (1999-12-23) page 1, line 1 -page 2, line 11 page 7, line 1 - line 4 page 7, line 20 - line 23 tables 12-15	1-11, 27, 29-32
A	page 5, line 38 -page 6, line 14; tables 66-78 --- US 5 030 271 A (ROBERT M. WATKINS) 9 July 1991 (1991-07-09) --- -/-	12-15, 20, 21, 23, 24, 26, 28
A		

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; RILEY, DENNIS G. ET AL: "Influence of imazapyr on the control of pitted morningglory (<i>Ipomoea lacunosa</i>) and johnsongrass (<i>Sorghum halepense</i>) with chlorimuron, imazaquin, and imazethapyr" retrieved from STN Database accession no. 110:35249 XP002257549 abstract & WEED SCIENCE (1988), 36(5), 663-6 ,</p> <p>---</p>	
A	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; RILEY, DENNIS G. ET AL: "Johnsongrass (<i>Sorghum halepense</i>) and pitted morningglory (<i>Ipomoea lacunosa</i>) control with imazaquin and imazethapyr" retrieved from STN Database accession no. 110:227082 XP002257550 abstract & WEED TECHNOLOGY (1989), 3(1), 95-8 ,</p> <p>-----</p>	

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/07983

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